

# PATENT SPECIFICATION

(11) 1300505

1300505

## NO DRAWINGS

- (21) Application No. 21168/71 (22) Filed 19 April 1971
- (31) Convention Application No. 1774 (32) Filed 6 Feb. 1970
- (31) Convention Application No. 178 (32) Filed 7 Jan. 1971 in
- (33) Switzerland (CH)
- (45) Complete Specification published 20 Dec. 1972
- (51) International Classification C08G 30/14//D06M 15/60
- (52) Index at acceptance



C3B 1C10 1C12 1C16 1C21 1C25 1C6X 1C8R 1D1B  
1D2A 1D2C 1D3 1D4X 1D6 1L2A 1L2X 1L5C  
1L6H 1N18X 1N1G 1N1X 1N2A 1N4C 1N5A  
1N6D1 1N6D4 1N6D7 1N6D8 1N6H 1N8A 1P  
D1P A1 A17 B4D C1H1X C2A12A7 C2A12AX C2C3  
C2C9  
D2B 36J1 36JX 36M1 36M2 36MY 41A

## (54) PREPARATIONS OF REACTION PRODUCTS OF EPOXIDES, FATTY AMINES AND BASIC POLYAMIDES, PROCESSES FOR THEIR MANUFACTURE AND THEIR USE

(71) We, CIBA-GEIGY AG, a Swiss Body Corporate of Basle, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

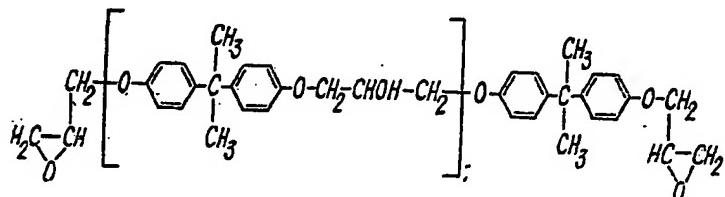
The present invention provides a process for the manufacture of stable preparations of water-soluble or water-dispersible reaction products of polyepoxides, fatty amines and basic polyamides, which comprises reacting a) a reaction product of a') at least one polyepoxide which contains at least two epoxide groups per molecule, and a'') at least one high-molecular weight fatty amine, such that the equivalent ratio of epoxide groups to amino groups is 1:0.1 to 1:0.85, with b) a basic polyamide which is obtained by condensation of b') polymeric, unsaturated fatty acids and b'') poly-alkylenepolyamines, in the presence of an organic solvent, at temperature of up to 95°C, such that the equivalent ratio of epoxide groups of the component a) to amino groups of the component b) is 1:1 to 1:6, with the addition of acid at some stages before completion of the reaction so that a sample of the reaction mixture has a  $p_{\text{II}}$  value of 2 to 8 after addition of water.

The expression "equivalent" as use herein means the amount of basic polyamide in grams which is equivalent to one mol of monoamine.

The epoxides a') from which the component a) is obtained are preferably derived from polyhydric phenols or polyphenols, such as resorcinol, and phenol-formaldehyde condensation products of the resol or novolak types. Bis-phenols such as bis-(4-hydroxyphenyl)-methane and especially 2,2-bis-(4'-hydroxyphenyl)-propane are the preferred starting compounds.

Particularly suitable as component a') are epoxides of 2,2-bis-(4'-hydroxyphenyl)-propane which have an epoxide content of 1.8 to 5.8 preferably at least 5 epoxide group equivalent/kg, and which correspond to the formula

(1)



wherein z has an average value of 0 to 0.65. These epoxides are obtained by reaction of epichlorohydrin with 2,2-bis-(4'-hydroxyphenyl)-propane.

Mono-fatty amines with 12 to 24 carbon atoms are particularly suitable as component a''). The preferred amines have the formula

(2)



wherein x represents an integer having a value of 11 to 23, preferably 17 to 21, for example, laurylamine, palmitylamine, stearylamine, arachidylamine or behenylamine. Mixtures of such amines, such as those obtainable as technical products, can also be used.

The reaction of the component a') with the component a'') may be performed at 80 to 120°C, preferably at 100°C.

The ratio of epoxides a') to amines a'') in the component a) is chosen such that there is an excess of epoxide, i.e. there is more than one epoxide group for each amino group, and the reaction products a) thus contain epoxide end groups. The equivalent ratio of epoxide groups of the components a') to amino groups of the component a'') is preferably 1:0.1 to 1:0.5, especially 1:0.25 to 1:0.5.

The polymeric unsaturated fatty acids used as the component b') for the manufacture of the basic polyamides b) are preferably aliphatic, ethylenically unsaturated dimeric to trimeric fatty acids. The reaction products b) are preferably manufactured from polyalkylenepolyamines b'') and aliphatic unsaturated dimeric to trimeric fatty acids b') which are derived from monocarboxylic acids with 16 to 22 carbon atoms, which have at least one, preferably 2 to 5, ethylenically unsaturated bonds, for example, oleic acid, hiragonic acid, elaeostearic acid, licanic acid, arachidonic acid, clupanodonic acid and, especially, linoleic acid and linolenic acid. These fatty acids can be obtained from natural oils, wherein they occur mainly as glycerides. The dimeric to trimeric fatty acids b') are obtained by dimerisation of the monocarboxylic acids using methods known per se. The so-called dimeric fatty acids always contain some trimeric acids and a small amount of monomeric acids.

The dimerised to trimerised linoleic or linolenic acids are particularly suitable for use as component b'). The technical products of these acids as a rule contain 75 to 95 per cent by weight of dimeric acid, 4 to 25 per cent by weight of trimeric acid and a trace of 3% of monomeric acid. The molar ratio of dimeric acid to trimeric acid is accordingly about 5:1 to 36:1.

Particularly suitable as components b'') are polyamines, such as diethylenetriamine, triethylenetetramine or tetrathylenepentamine, i.e., amines of the formula

(3)



wherein n is 1, 2 or 3.

In the case of amine mixtures, it is also possible for n to have a non-integral average value, for example between 1 and 2.

The preferred basic polyamide b) is that derived from dimerised to trimerised linoleic or linolenic acid and a polyamine of the formula (3).

The reaction of the component a) with b) may take place in the presence of water-soluble organic solvents, especially those which are miscible with water to an unlimited extent, for example dioxane, isopropanol, ethanol and methanol, ethylene glycol n-butyl ether (=n-butylglycol), and diethylene glycol monobutyl ether.

The reaction can also be carried out in the presence of water-insoluble organic solvents, for example in petrol hydrocarbons such as petrol or petroleum ether, benzene, or benzenes which are halogenated or substituted by lower alkyl groups, such as toluene, xylene or chlorobenzenes; alicyclic compounds such as tetralin or cyclohexane; and halogenated hydrocarbons such as methylene chloride, methylene bromide, chloroform, carbon tetrachloride, ethylene chloride, ethylene bromide, s-tetrachloroethane and especially trichloroethylene or perchloroethylene.

The reaction products thus obtained are soluble, or at least dispersible, in water.

A third component c), namely a further monofunctional or difunctional compound which is different from a) and b) may be used in conjunction with components a) and b). These monofunctional or difunctional compounds may possess mobile halogen atoms, or vinyl, acid, ester, acid anhydride, isocyanate or epoxide groups as functional groups or atoms. Preferably, about 0.25 mol of a monofunctional compound c) are used per one amino group equivalent of the component b) but this content may be increased up to, for example, 0.5 mol per amino group equivalent. If difunctional compounds are

used, preferably 0.05 to 0.5 mol are employed per one amino group equivalent of the component b).

These components c) are preferably aralkyl or alkyl halides, nitriles or amides of acids of the acrylic acid series, aliphatic or aromatic carboxylic acids, their esters or anhydrides, and aliphatic or aromatic isocyanates, epoxides or epihalogenohydrins.

Suitable monofunctional compounds are alkyl halides such as ethyl bromide or butyl chloride, aralkyl halides such as benzyl chloride; nitriles or amides of acrylic acid or methacrylic acid such as acrylonitrile or acrylic acid amide; alkanecarboxylic acids with up to 18 carbon atoms such as coconut fatty acid or stearic acid, or their esters with alkanols which contain at most 5 carbon atoms, for example methanol, ethanol or n-butanol, or their anhydrides such as acetic anhydride; aromatic isocyanates such as phenyl isocyanate, or aliphatic or aromatic epoxides such as propylene oxide, butylene oxide, dodecene oxide or styrene oxide. The preferred difunctional component c) is epichlorohydrin.

Particularly suitable components c) are alkylene oxides with at most 12 carbon atoms, alkanecarboxylic acids with at most 18 carbon atoms, monocyclic aralkyl halides or acrylonitrile.

The reaction of the polyamides with the monofunctional compounds and epoxide-fatty amine reaction products may take place in any order. The polyamide can be reacted first with a monofunctional compound and then with the epoxide-fatty amine reaction product, or vice versa. In some cases, if there are no great differences in the reactivity, the reaction can also be carried out simultaneously.

The reaction to give the reaction product of the components a) and b) is carried out in such a way that polyaddition products which are soluble or dispersible in water are produced, by adjusting the  $p_{\text{H}}$  value, at some stage before completion of the reaction, to 2 to 8, preferably to 2 to 7, especially to 5 to 6. Inorganic or organic acids, especially relatively volatile organic acids such as formic acid or acetic acid may be used for this purpose. It is advisable to add a certain amount of acid to the reaction mixture immediately at, or shortly after, the beginning of the reaction of the polyamide with the epoxide, and also to add further acid continuously or in portions during the further reaction. Furthermore, the process is preferably carried out at temperatures of up to 80°C, for example of 25 to 80°C, especially 45 to 70°C. The resulting solutions or dispersions, which are, in most cases, slightly opalescent to cloudy solutions, which have been adjusted with acid to the desired  $p_{\text{H}}$  value, and which have been diluted by means of an organic solvent, or preferably by means of water, so that they constitute, 10 to 30% of the reaction product, are distinguished by high stability.

Products with desirable properties are also obtained if after the addition of the acid and of the water, the preparation is further stored at room temperature or elevated temperature, for example for 4 hours at 70°C or for a longer period at a lower temperature.

The products of the invention are suitable for finishing textiles, especially for rendering wool non-felting, in which case the wool may be impregnated with an aqueous liquor to which the preparation and, if desired, yet further additives such as wetting agents, dispersing agents and/or acids or bases have been added, then dried and subjected to a treatment at elevated temperature, (i.e. at a temperature above room temperature and below that at which the materials may be damaged during the treatment; suitable temperatures are in the range 40 to 120°C). In particular, the process for rendering wool non-felting, may be carried out in conjunction with a dyeing process. In this way, dyeing and rendering non-felting can be combined in a simple manner and carried out in the same apparatus without the wool being taken out of the apparatus between the two processes.

In the exhaustion method for rendering wool non-felting, the wool is treated at temperatures of 35 to 100°C and a pH of 7 to 10 with the epoxide/polyamide reaction product. The liquor used for rendering the wool non-felting may contain, in addition to the polyaddition product, an amount of base, for example, ammonia, disodium phosphate or trisodium phosphate, sufficient to give the required alkalinity. The amount of polyaddition product (not counting solvents and water), relative to the weight of the wool, is generally 0.5 to 5%. Between 20 and 80 minutes is usually required for extensive to practically complete fixing of the polyaddition product.

Treatment of wool to render it non-felting can also be carried out using a padding process in which the liquor has a pH of 3 to 7. The required acidity can be achieved by the addition of, for example, low molecular weight aliphatic carboxylic acids.

Dyeing can be carried out using methods and dyestuffs known *per se* for the dyeing of wool, for example, acid wool dyestuffs, 1:1 or 1:2 metal complex dyestuffs or reactive dyestuffs. Additives customarily used in processes for dyeing wool, such as

sulphuric acid, acetic acid, sodium sulphate, ammonium sulphate and levelling agents, especially polyglycol compounds of higher aliphatic amines, which can optionally also be quaternised and/or esterified at the hydroxy groups by polybasic acids, may also be used.

5 The sequence of the two processes is optional but it is generally preferable to carry out the dyeing first and the non-felting treatment afterwards.

The combined process for dyeing wool and rendering it non-felting is particularly suitable for use in actual machine dyeing, where the goods being dyed are static and the liquor is agitated.

10 Oxidising agents, such as hydrogen peroxide may also be added to the treatment baths. If desired, the permanence of the non-felting finishes can be improved by pre-treating the wool with a dilute aqueous solution of dichloroisocyanurate acid or its alkali metal salt before the wool is treated with the preparation containing the epoxide polyamide reaction product.

15 If treatment baths with a high content of organic, particularly water-insoluble, solvents, or even anhydrous baths containing only organic solvents, are used, the process is appropriately carried out in closed apparatuses, for example of the type used in dry cleaning.

20 Treatment with the preparations of the invention improves the fixing of dyestuffs, especially reactive dyestuffs to textiles, especially wool, resulting in an improved fastness to perspiration. Mechanical properties, for example tear strength, elongation at break, abrasion resistance, and tendency to pilling, of the treated textile material are also improved.

25 When the preparations are used in combination with an aminoplast pre-condensate on textiles, especially cotton, a wash-resistant "soil release" effect is achieved. It is also possible to manufacture textiles with a so-called non-iron finish using the preparations of the invention.

The preparations of the invention may also be used as sizing agents for paper.

30 In some cases, the epoxide/polyamide reaction products may be used as a solution or as a dispersion in an organic solvent. Suitable solvents are those described for the manufacturing processes.

35 When the reaction products are insoluble in water-insoluble organic solvents, they can be dispersed in the water-insoluble solvent in the presence of an organo-soluble surface-active agent. For this purpose the reaction product, the solvent and the surface-active agent can be mixed with stirring, or, preferably, the reaction product can be worked into a paste with the surface-active agent and then introduced into the solvent, with stirring to give a stable dispersion.

This dispersion may be applied in the same way as described for the aqueous preparations.

40 In the manufacturing instructions and examples which follow, the percentages are percentages by weight.

#### Manufacturing Instructions

A) 196 g (1 epoxide group equivalent) of a polyepoxide formed from 2,2-bis-(4'-hydroxyphenyl)-propane and epichlorohydrin, together with 31 g (0.1 amino group equivalent) of a mixture of 1-amino-eicosane and 1-amino-docosane, are stirred for one hour at 130°C. A clear, viscous product with an epoxide group equivalent weight of 255 is obtained.

45 B) 196 g (1 epoxide group equivalent) of the polyepoxide described under A), together with 62 g (0.2 amino group equivalent) of the fatty amine mixture described under A), are stirred for one hour at 100°C. A clear, viscous product with an epoxide group equivalent weight of 313 is obtained.

C) 196 g (1 epoxide group equivalent) of the polyepoxide described under A), together with 77.5 g (0.25 amino group equivalent) of the fatty amine mixture described under A), are stirred for one hour at 100°C. A highly viscous product with an epoxide group equivalent weight of 379 is obtained.

50 D) 196 g (1 epoxide group equivalent) of the polyepoxide described under A), together with 93 g (0.3 amino group equivalent) of the fatty amine mixture described under A), are stirred for one hour at 100°C. A highly viscous product with an epoxide group equivalent weight of 436 is obtained.

E) 196 g (1 epoxide group equivalent) of the polyepoxide described under A), together with 108.5 g (0.35 amino group equivalent) of the fatty amine mixture described under A), are stirred for one hour at 100°C. A highly viscous product with an epoxide group equivalent weight of 498 is obtained.

F) 196 g (1 epoxide group equivalent) of the polyepoxide described under A) together

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with 124 g (0.4 amino group equivalent) of the fatty amine mixture described under A), are stirred for one hour at 100°C. A highly viscous product with an epoxide group equivalent weight of 507 is obtained.

5 G) 196 g (1 epoxide group equivalent) of the polyepoxide described under A), together with 155 g (0.5 amino group equivalent) of the fatty amine mixture described under A), are stirred for one hour at 100°C. A highly viscous product with an epoxide group equivalent weight of 685 is obtained.

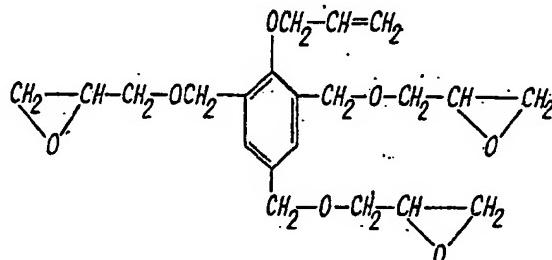
10 H) 91.2 g of butanediol diglycidyl ether (0.8 epoxide group equivalent), together with 62 g (0.2 amino group equivalent) of a mixture of 1-amino-eicosane and 1-amino-docosane, are stirred for one hour at 100°C. A clear, viscous product with an epoxide group equivalent weight of 257 is obtained.

15 I) 99 g of hexahydrophthalic acid diglycidyl ester (0.6 epoxide group equivalent), together with 46.5 g (0.15 amino group equivalent) of a mixture of 1-amino-eicosane and 1-amino-docosane are stirred for one hour at 100°C. A clear, viscous product with an epoxide group equivalent weight of 395 is obtained.

20 J) 98 g of a polyepoxide formed from 2,2-bis-(4'-hydroxyphenyl)-propane and epichlorohydrin (0.5 epoxide group equivalent), together with 33.7 g of stearylamine (0.125 amino group equivalent), are stirred for 1 hour at 100°C. A clear, viscous product with an epoxide group equivalent of 400 is obtained.

K) 96 g of a triepoxide of the formula

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(4)



(0.6 epoxide group equivalent) together with 46.5 g (0.15 amino group equivalent) of a mixture of 1-amino-eicosane and 1-amino-docosane, are stirred for 1 hour at 100°C. A clear, viscous product with an epoxide group equivalent weight of 278 is obtained.

25 L) 99.6 g of triglycidyl isocyanurate (0.6 epoxide group equivalent), together with 46.5 g (0.15 amino group equivalent) of a mixture of 1-amino-eicosane and 1-amino-docosane, are stirred for 1 hour at 100°C. A clear product with an epoxide group equivalent weight of 208 is obtained.

30 M) 156.8 g of a polyepoxide formed from 2,2-bis-(4'-hydroxyphenyl)-propane and epichlorohydrin (0.8 epoxide group equivalent), together with 37.1 g of laurylamine (0.2 amino group equivalent), are stirred for 1 hour at 100°C. A clear product with an epoxide group equivalent weight of 403 is obtained.

35 N) 98 g of a polyepoxide formed from 2,2-bis(4'-hydroxyphenyl)-propane and epichlorohydrin (0.5 epoxide group equivalent) are warmed to 85 to 90°C, 124 g (0.4 amino group equivalent) of a mixture of 1-amino-eicosane and 1-amino-docosane is then added over the course of 15 minutes. Thereafter the mixture is stirred for a further 6 hours at 100°C. A highly viscous product with an epoxide group equivalent weight of 2220 is obtained.

40 O) 196 g of a polyepoxide formed from 2,2-bis-(4'-hydroxyphenyl)-propane and epichlorohydrin (1 epoxide group equivalent), together with 32 g of lauryl-propylene-diamine (0.2 amine equivalent), are stirred for 1 hour at 100°C. A clear product with an epoxide group equivalent weight of 380 is obtained.

45 P) 196 g of a polyepoxide formed from 2,2-bis-(4'-hydroxyphenyl)-propane and epichlorohydrin (1 epoxide group equivalent), together with 20.4 g of all oil propylene-diamine (0.1 amine equivalent), are stirred for 1 hour at 100°C. A clear product with an epoxide group equivalent weight of 282 is obtained.

Tall oil-propylene diamine is a reaction product of propylene-diamine with "tall oil", which is a mixture containing fatty acids, which is recovered in the manufacture of paper from wood pulp. The composition is variable depending on the type of wood used, but generally includes a large amount of oleic and linoleic acids.

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Example 1  
49.4 g of a polyamide of polymerised linoleic acid and diethylenetriamine (0.2

5 amino group equivalent) are dissolved in 50 g of butylglycol and warmed to 53°C. A solution of 18.95 g of the polyepoxide/amine reaction product C) (0.05 epoxide group equivalent) in 20 g of n-butylglycol is then run in dropwise over the course of 30 minutes. One hour thereafter, a solution of 8 g of glacial acetic acid in 195 g of deionised water is added and the mixture is further stirred until cold. A mobile solution of solids content 20% and pH value 7.0 is obtained.

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#### Example 2

10 49.4 g (0.2 amino group equivalent) of the polyamide used in Example 1 are dissolved in 50 g of n-butylglycol and warmed to 58°C. A solution of 34.25 g of the polyepoxide/amine reaction product G) (0.05 epoxide group equivalent) and 35 g of n-butylglycol is then run in dropwise over the course of 40 minutes. One hour thereafter, a solution of 7 g of glacial acetic acid in 226 g of deionised water is added and the mixture is stirred until cold. A viscous solution of solids content 20% and pH value 7.0 is obtained.

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15 61.8 g of a polyamide of polymerised linoleic acid and diethylenetriamine (0.25 amino group equivalent) are dissolved in 61.8 g of isopropanol and warmed to 53°C. A solution of 12.85 g of the polyepoxide/amine reaction product H) (0.55 epoxide group equivalent) in 12.85 g of isopropanol is then added dropwise over the course of 30 minutes. One hour thereafter, a solution of 15 g of glacial acetic acid in 200 g of deionised water is added and the mixture is further stirred until cold. A mobile solution of solids content 20% and pH value 6.0 is obtained.

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#### Example 3

20 49.4 g (0.2 amino group equivalent) of the polyamide used in Example 3 are dissolved in 49.4 g of ethanol and warmed to 53°C. A solution of 19.8 g of the polyepoxide/amine reaction product I) (0.05 epoxide group equivalent) in 19.8 g of ethanol is then added dropwise over the course of 30 minutes. One hour thereafter, 24 g of glacial acetic acid in 180 g of deionised water are added and the mixture is further stirred until cold. A clear, mobile solution of solids content 20% and pH value 5.9 is obtained.

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25 49.4 g (0.2 amino group equivalent) of the polyamide used in Example 3 are dissolved in 49.4 g of butylglycol and warmed to 54°C. A solution of 20 g of the polyepoxide/amine reaction product J) (0.05 epoxide group equivalent) in 20 g of butylglycol is then added dropwise over the course of 30 minutes. One hour thereafter, 12 g of glacial acetic acid in 190 g of deionised water are added and the mixture is further stirred until cold. A clear, mobile solution of solids content 20% and pH value 5.4 is obtained.

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30 49.4 g (0.2 amino group equivalent) of the polyamide used in Example 3 are dissolved in 49.4 g of dioxane and warmed to 55°C. A solution of 13.9 g of the polyepoxide/amine reaction product K) (0.05 epoxide group equivalent) in 13.9 g of dioxane is then run in dropwise over the course of 30 minutes.

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35 49.4 g (0.2 amino group equivalent) of the polyamide used in Example 3 are dissolved in 49.4 g of dioxane and warmed to 55°C. A solution of 13.9 g of dioxane is then run in dropwise over the course of 30 minutes. One hour thereafter, 12 g of glacial acetic acid in 172 g of deionised water are added and the mixture is further stirred until cold. A mobile solution of solids content 20% and pH value 5.4 is obtained.

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#### Example 6

40 49.4 g (0.2 amino group equivalent) of the polyamide used in Example 3 are dissolved in 49.4 g of dioxane and warmed to 55°C. A solution of 13.9 g of the polyepoxide/amine reaction product K) (0.05 epoxide group equivalent) in 13.9 g of dioxane is then run in dropwise over the course of 30 minutes.

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45 One hour thereafter, 12 g of glacial acetic acid in 172 g of deionised water are added and the mixture is further stirred until cold. A mobile solution of solids content 20% and pH value 5.4 is obtained.

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#### Example 7

50 79 g (0.32 amino group equivalent) of the polyamide used in Example 3 are dissolved in 79 g of butylglycol and warmed to 55°C. A solution of 16.6 g of the polyepoxide/amine reaction product L) (0.08 epoxide group equivalent) and 16.6 g of butylglycol is then run in dropwise over the course of 30 minutes. 40 minutes thereafter, 19.2 g of glacial acetic acid and 260 g of deionised water are added and the mixture is further stirred until cold. A mobile solution of solids content 20% and pH value 5.6 is obtained.

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#### Example 8

55 a) 187 g of polymerised fatty acid and 68.5 g of diethylene-triamine are introduced into a reaction vessel which is provided with a stirrer, thermometer, nitrogen inlet tube and distillation head. The polymerised fatty acid, obtained by polymerisation of oleic

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acid, has the following properties: 95% dimerised oleic acid; equivalent weight: 289.

The reaction mixture is heated with stirring to 200°C over the course of 1½ hours under a nitrogen atmosphere and under these conditions the splitting-off of water starts at 160°C. After a further 2 hours at 200°C, a total of 13 parts of water are collected. Thereafter the mixture is concentrated for 3 hours *in vacuo* (14 mm Hg) at 200 to 210°C. 210 g of a viscous, yellowish, clear product with an amine equivalent weight of 372 are obtained.

b) 74.4 g of the condensation product described under a) (0.2 amino group equivalent) are dissolved in 74.4 g of butylglycol and warmed to 55°C. A solution of 20.2 g of the polyepoxide/amine reaction product M) (0.05 epoxide group equivalent) and 20.2 g of butylglycol is then run in dropwise over the course of 30 minutes. 30 minutes thereafter, 12 g of glacial acetic acid and 265 g of deionised water are added and the mixture is further stirred until cold. A clear, mobile solution of solids content 20% and  $p_{\text{H}}$  value 6.0 is obtained.

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#### Example 9

44.6 g of the condensation product described under 8a) (0.12 amino group equivalent) are dissolved in 44.6 g of butylglycol and warmed to 60°C. 7.2 g of glacial acetic acid and a solution of 44.4 g of the polyepoxide/amine reaction product N) (0.02 epoxide group equivalent) and 44.4 g of butylglycol are then run in dropwise over the course of 30 minutes from 2 separate dropping funnels. Thereafter the mixture is stirred for a further 6½ hours at 60°C, and a further 10 g of glacial acetic acid are then added. After a further 30 minutes, the mixture is diluted with 180 g of butylglycol. A clear, mobile solution of solids content 20% is obtained.

A sample diluted with water, 1:20, shows a  $p_{\text{H}}$  value of 5.8.

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#### Example 10

66.6 g of the polyepoxide/amine reaction product N) (0.03 epoxide group equivalent) are dissolved in 66.6 g of butylglycol and warmed to 60°C. 5.6 g of glacial acetic acid and a solution of 33.4 g of the condensation product described under 8a) (0.09 amino group equivalent) and 33.4 g of butylglycol are then run in dropwise over the course of 30 minutes from 2 separate dropping funnels.

The mixture is then stirred for a further 6½ hours at 60°C, and a further 10 g of glacial acetic acid are then added. After a further 30 minutes, the mixture is diluted with 283 g of butylglycol. A clear, mobile solution of solids content 20% is obtained. A sample diluted with water, 1:20, shows a  $p_{\text{H}}$  value of 5.8.

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#### Example 11

68.5 g of the polyepoxide/amine reaction product G) (0.1 epoxide group equivalent) are dissolved in 37 g of isopropanol and warmed to 88°C. A solution of 24.7 g (0.1 amino group equivalent) of the polyamide used in Example 3 and 15 g of isopropanol is then run in dropwise over the course of 30 minutes.

The mixture is then stirred for a further 5 hours at approx. 88°C (reflux), and 1.85 g of epichlorohydrin (0.02 mol) are then added. After a further 10 minutes, a solution of 16 g of glacial acetic acid and 312 g of deionised water is added and the mixture is further stirred until cold. A mobile product of solids content 20% and  $p_{\text{H}}$  value 4.6 is obtained.

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#### Example 12

79 g (0.32 amino group equivalent) of the polyamide used in Example 3 are dissolved in 40 g of butylglycol and warmed to 80°C. A solution of 30.4 g of the polyepoxide/amine reaction product O) (0.08 epoxide group equivalent) and 30.4 g of butylglycol is then run in dropwise over the course of 30 minutes.

15 minutes thereafter, 20 g of glacial acetic acid and 336 g of deionised water are added and the mixture is further stirred until cold. A mobile solution of solids content 20% and  $p_{\text{H}}$  value 5.3 is obtained

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Example 13  
79 g (0.32 amino group equivalent) of the polyamide used in Example 3 are dissolved in 40 g of butylglycol and warmed to 80°C. A solution of 22.6 g of the polyepoxide/amine reaction product P) and 22.6 g of butylglycol is then run in dropwise over the course of 30 minutes.

15 minutes thereafter, 20 g of glacial acetic acid and 311 g of deionised water are added and the mixture is further stirred until cold. A mobile solution of solids content 20% and  $p_{\text{H}}$  value 5.2 is obtained.

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**Example 14**

79 g (0.32 amino group equivalent) of the polyamide used in Example 3 are warmed to 180°C. 16.7 g of dodecene oxide (0.08 mol) are run in dropwise over the course of 2 hours, the mixture is kept at 180°C for a further 2 hours and then cooled to 50°C., and the product is dissolved in 32 g of butylglycol. A solution of 20.4 g of the polyepoxide/amine reaction product A) (0.08 epoxide group equivalent) and 20.4 g of butylglycol is then run in dropwise over the course of 30 minutes at 50°C. The temperature is then raised to 60°C and the mixture is stirred for a further 1½ hours at this temperature. 20 g of glacial acetic acid and 391 g of deionised water are then added and the mixture is further stirred until cold. A mobile solution of solids content 20% and a pH value of 4.9 is obtained.

**Example 15**

79 g (0.32 amino group equivalent) of the polyamide used in Example 3, together with 10.1 g of benzyl chloride (0.08 mol), are stirred for 2 hours at 100°C. The product is then cooled to 60°C and 32 g of butylglycol are added. A solution of 20.4 g of the polyepoxide/amine reaction product A) (0.08 epoxide group equivalent) and 20.4 g of butylglycol is then run in dropwise at this temperature over the course of 30 minutes. 25 minutes thereafter, 20 g of glacial acetic acid and 364 g of deionised water are added and the mixture is further stirred until cold. A mobile solution of solids content 20% and pH value 4.6 is obtained.

**Example 16**

79 g (0.32 amino group equivalent) of the polyamide used in Example 3 are dissolved in 32 g of butylglycol and warmed to 50°C. 4.3 g of acrylonitrile (0.08 mol) are then added and the mixture is stirred for 2 hours at 50°C. A solution of 20.4 g of the polyepoxide/amine reaction product A) (0.08 epoxide group equivalent) and 20.4 g of butylglycol is then run in dropwise over the course of 30 minutes. 1½ hours thereafter, 20 g of glacial acetic acid and 339 g of deionised water are added and the mixture is further stirred until cold. A mobile solution of solids content 20% and pH value 5.0 is obtained.

**Use Examples****Example 17**

100 kg of wool yarn are dyed in the customary manner with reactive dyestuffs in 1000 litres of water in a cheese-dyeing apparatus. After dyeing, the yarn is thoroughly rinsed.

A fresh bath at 40°C, consisting of 1000 litres of water and 1.4 kg of ammonia (25% strength) is prepared. Thereafter, 8 kg of the product according to Example 1 are added. A stable emulsion forms, which is uniformly absorbed on the wool in about 30 minutes. Trisodium phosphate is then added, the process is allowed to continue for 10 minutes, and 2 kg of a 12.5% strength solution of a condensation product of 1 mol of octadecyl alcohol and 25 mols of ethylene oxide are further added. After a further 20 minutes the yarn is thoroughly rinsed with cold water, drained and dried. The yarn treated in this way is non-felting according to IWS specifications 7B, 7C and 71.

Instead of a product according to Example 1, a product of any one of the Examples 2 to 16 can be used with equally good results.

**Example 18**

A woven fabric of pure wool is impregnated with the following preparation, and subjected to a liquor uptake of 100% on a horizontal two-roll padder:

120 g/l of the product according to Example 1  
 2 g/l of a condensation product of  
 1 mol of p-tert.-octylphenol and  
 8 mols of ethylene oxide  
 30 ml/l of 33% strength hydrogen peroxide  
 848 ml/l of water

1000 g of padding liquor.

After padding, the goods are dried on a stenter frame. They are then pressed for 5 minutes at 120°C under medium press pressure (on a "Hoffmann [Registered Trade Mark] press").

The goods thus treated show the following shrinkage values on testing according to IWS Specification 71:

untreated goods	53% shrinkage
treated goods	2.1% shrinkage

5 If, before the treatment just described, the fabric is additionally subjected to the known reductive treatment with monoethanolamine sulphite, the goods are additionally surface-stable, that is to say they remain smooth and free from creases even after washing.

5

#### Example 19

10 3.0 g of a preparation according to Example 1 are worked into a paste with 10.0 g of a surface-active agent of the composition given below, and this mixture is diluted to 1000 ml with perchloroethylene. Brief stirring yields a stable dispersion. 20 g of a knitted woollen piece are treated with this liquor for 50 minutes at 20°C. After removing excess liquor by centrifuging, the piece is dried and fixed for 10 minutes at 100°C.

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15 The treated knitted pieces are non-felting.

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The following products are used as surface-active agents:

I: Condensation product of 1 mol of coconut fatty acid and 2 mols of diethanolamine, containing about 2% of water and about 2% of acetic acid.

20 II: Acid phosphoric acid ester of a condensation product of 1 mol of 2-ethylhexanol and 5 mols of ethylene oxide, neutralised with sodium hydroxide, in the form of an 80% strength aqueous solution.

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III: Aqueous solution containing: 38.5% of an oleic acid of a polyglycol ester, 38.5% of a condensation product of 1 mol of p-tert.-octylphenol and 8 mols of ethylene oxide, and 15.5% of oleic acid.

#### Example 20

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25 100 kg of bleached sulphite cellulose are ground in the usual manner in a holander and subsequently discharged into a mixing vessel. 20 kg of calcium carbonate are added as a filler in the mixing vessel. When the filler has become well distributed in the pulp suspension, 0.3 to 0.7% of the product according to Example 11, relative to cellulose and solids content, is added. The pulp mixture passes through the paper machine via further stages of the process of paper manufacture.

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30 To increase the filler retention, a retention agent can be added shortly before running the pulp onto the machine.

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35 Papers manufactured with this or a similar pulp composition are predominantly used as writing papers and printing papers and show excellent ink resistance, resulting from the good sizing.

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Aluminium sulphate, which is introduced into this system when waste paper is incorporated, does not interfere in any way with the sizing.

40 In this system, the calcium carbonate can also be replaced by commercially available kaolin. The sizing effect is the same as when using calcium carbonate.

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#### WHAT WE CLAIM IS:—

1. A process for the manufacture of stable preparations of water-soluble or water-dispersible reaction products of polyepoxides, fatty amines and basic polyamides, which comprise reacting a) a reaction product of a') at least one polyepoxide which contains at least two epoxide groups per molecule, and a'') at least one high-molecular weight fatty amine, such that the equivalent ratio of epoxide groups to amino groups is 1:0.1 to 1:0.85, with b) a basic polyamide which is obtained by condensation of b') polymeric unsaturated fatty acids and b'') polyalkylenepolyamines, in the presence of an organic solvent, at temperatures of up to 95°C, such that the equivalent ratio of epoxide groups of the component a) to amino groups of the component b) is 1:1 to 1:6, with the addition of acid at some stage before completion of the reaction so that a sample of the reaction mixture has a pH value of 2 to 8 after addition of water.

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2. A process according to Claim 1, wherein the equivalent ratio of epoxide groups of the components a') to amino groups of the component a'') is 1:0.1 to 1:0.5.

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3. A process according to Claim 1 or 2, wherein the equivalent ratio of epoxide groups of the component a) to amino groups of the component b) is 1:1 to 1:5.

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4. A process according to any of the preceding Claims wherein the epoxide a') is derived from a bisphenol.

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5. A process according to Claim 4, wherein the epoxide a') is a polyglycidyl ether

of 2,2-bis-(4'-hydroxyphenyl)-propane which has an epoxide content of 1.8 to 5.8 epoxide group equivalents/kg.

6. A process according to Claim 5, wherein the component a') has an epoxide content of at least 5 epoxide group equivalents per kg.

5 7. A process according to Claim 5 or 6, wherein the component a') is obtained by reaction of epichlorohydrin with 2,2-bis-(4'-hydroxyphenyl)-propane.

8. A process according to any of the preceding Claims wherein the component a'') is a mono-fatty amine with 12 to 24 carbon atoms.

9. A process according to Claim 8, wherein the fatty amine has the formula

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wherein x is an integer having a value of 11 to 23.

10. A process according to Claim 9, wherein x is 17 to 21.

11. A process according to any of the preceding Claims wherein component b') is an aliphatic, ethylenically unsaturated dimeric to trimeric fatty acid or a mixture of such acids.

15 12. A process according to Claim 11, wherein the fatty acids are derived from aliphatic unsaturated mono-carboxylic acids with 16 to 22 carbon atoms.

13. A process according to Claim 12, wherein the component b') is dimerised to trimerised linoleic acid or linolenic acid.

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14. A process according to any of the preceding Claims wherein the component b'') is an aliphatic polyamine of the formula

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wherein n is 1, 2 or 3.

25 15. A process according to any of the preceding Claims wherein the reaction takes place in an organic solvent which is miscible with water to an unlimited extent.

16. A process according to any of the preceding Claims wherein the reaction is carried out at 25 to 80°C.

17. A process according to Claim 16, wherein the reaction is carried out at 45 to 70°C.

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18. A process according to any of the preceding claims wherein a monofunctional or difunctional compound c) which differs from a) and b) is used in conjunction with the components a) and b).

19. A process according to Claim 18, wherein the component c) is an epihalogenohydrin.

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20. A process according to Claim 1 substantially as hereinbefore described.

21. A process according to Claim 1 substantially as described in Example 1 or 2.

22. A process according to Claim 1 substantially as described in any of Examples 3 to 16.

40 23. Water-soluble or water-dispersible reaction products of polyepoxides, fatty amines and basic polyamides when obtained by a process according to any of Claims 1 to 21.

24. Water-soluble or water-dispersible reaction products of polyepoxides, fatty amines and basic polyamides when obtained by a process according to Claim 22.

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25. A process for finishing textiles which comprises treating the textiles with a preparation which contains a reaction product as claimed in Claim 23 or 24.

26. Textiles when treated by a process according to Claim 25.

27. A process for rendering wool non-felting which comprises impregnating the wool with an aqueous liquor containing a reaction product as claimed in Claim 23 or 24, dyeing the wool and subjecting it to a heat treatment at 40° to 120°C.

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28. A process according to Claim 27, wherein an exhaustion process is used in which the wool is treated at temperatures of 35° to 100°C with an aqueous liquor containing a reaction product as claimed in Claim 23 or 24 and having a pH of 7 to 10.

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29. A process according to Claim 27 wherein a padding process is used in which the wool is treated with an aqueous liquor containing a reaction product as claimed in claim 23 or 24 and having a pH of 3 to 7.

30. A process according to Claim 29 wherein, the aqueous liquor contains a low molecular weight carboxylic acid.

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31. A process for finishing wool in which a process for rendering wool non-felting as claimed in any of claims 27 to 30 is carried out in conjunction with a dyeing process.
32. Woollen goods whenever treated by a process according to any of claims 27 to 31.

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Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1972.  
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from  
which copies may be obtained.